

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

Dobson, Kevin S.  
E.I. DUPONT DE NEMOURS AND COMPANY  
Legal Patent Records Center  
4417 Lancaster Pike  
Wilmington, Delaware 19805  
ETATS-UNIS D'AMERIQUE

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NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing  
(day/month/year)

05.10.2004

☐ TO BE REVIEWED  
BY ATTORNEY

Applicant's or agent's file reference  
AD6899PCT

## IMPORTANT NOTIFICATION

International application No.  
PCT/US 03/24116

International filing date (day/month/year)  
31.07.2003

Priority date (day/month/year)  
31.07.2002

Applicant  
E.I. DU PONT DE NEMOURS AND COMPANY ET AL.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

**EEL NOTED**

31 JAN 2005

Name and mailing address of the international preliminary examining authority:



European Patent Office  
D-80298 Munich  
Tel. +49 89 2399 - 0 Tx: 523656 epmu d  
Fax: +49 89 2399 - 4465

Authorized Officer

Hoogland, J

Tel. +49 89 2399-2087



# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AD6899PCT	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/US 03/24116	International filing date ( <i>day/month/year</i> ) 31.07.2003	Priority date ( <i>day/month/year</i> ) 31.07.2002
International Patent Classification (IPC) or both national classification and IPC B41M5/00		
Applicant E.I. DU PONT DE NEMOURS AND COMPANY ET AL.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of    sheets.

3. This report contains indications relating to the following items:

- I    ☒ Basis of the opinion
- II   ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV   ☐ Lack of unity of invention
- V    ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI   ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand  23.02.2004	Date of completion of this report  05.10.2004
Name and mailing address of the international preliminary examining authority:  <div style="margin-left: 20px;"> European Patent Office  D-80298 Munich  Tel. +49 89 2399 - 0 Tx: 523656 epmu d  Fax: +49 89 2399 - 4465 </div>	Authorized Officer  Spyropoulou, E  Telephone No. +49 89 2399-2843 <div style="text-align: right;">  </div>

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/US 03/24116

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*):

**Description, Pages**

1-11 as originally filed

**Claims, Numbers**

1-22 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/US 03/24116

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	9-15,21,22
	No: Claims	1-7,20
Inventive step (IS)	Yes: Claims	
	No: Claims	1-8,16,20
Industrial applicability (IA)	Yes: Claims	1-22
	No: Claims	

**2. Citations and explanations**

**see separate sheet**

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

D1: EP-A-1114734

D2: JP(A) 2000355163 and its computerised English translation

1). From D1 and D2, a layer is known which is printed by ink jet, said layer described as "protective layer" and being a rigid elastomer for example an ethylene-acrylic rubber or butyl rubber (see D1, paragraph 435 and D2 abstract) and having the rigidity characteristics measured according to Young's Modulus and the thickness as defined in claim 1 of the present application (see D1, paragraphs 438 and 442 and D2, paragraphs 26,27).

A process for ink-jet printing an image on a rigid thermoplastic "interlayer" according to claim 1 and a thermoplastic "interlayer sheet" bearing an ink-jet printed image according to claim 20 are already disclosed in D1 and D2 and therefore not novel.

Claim 8 defines a process for obtaining a decorative laminate comprising the steps of laminating an ink jet printed interlayer sheet according to claim 1, between sheets of transparent materials to obtain a decorative laminate.

It is however a common measure in the art to protect a printed matter by laminating a transparent material on one or both of its surfaces.

The idea of laminating an ink jet printed matter between two transparent materials and thus the subject matter of claim 8 does not therefore involve an inventive step.

2). Dependent claims 2-7, 21 and 22 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step in view of the teachings of D1 and D2.

Moreover claim 22 defines the interlayer by the change of size of the image after drying. This is a definition of the interlayer by the result to be achieved leading to lack of clarity of said claim 22 (see PCT/GL/ISPE/1 5.35).

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/US 03/24116

3). The process for obtaining a decorative laminate according to claim 9 differs from the disclosure of D1 and D2 in that the rigid interlayer comprises a roughened surface having a roughness (Rz) of from 5  $\mu\text{m}$  to 15  $\mu\text{m}$  prior to lamination.

The subject matter of claim 9 and of claims 10-15, said claims depending on claim 9, appears to contain features which, if combined with the subject matter of claim 8 on which the above mentioned claims depend on, would meet the requirements of the PCT in respect of novelty and/or inventive step.

## NOTICES \*

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 \*\*\*\* shows the word which can not be translated.  
 In the drawings, any words are not translated.

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 LAIMS
 

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Claim(s)]

Claim 1] The ink-jet record sheet which has the 2nd layer prepared so that the 1st layer and this which are prepared on the base material might be touched, and is characterized by the Young's modulus of the 1st layer being lower than the Young's modulus of the 2nd layer.

Claim 2] The ink-jet record sheet according to claim 1 characterized by the 1st layer being an under-coating layer.

Claim 3] The ink-jet record sheet according to claim 1 or 2 characterized by the 2nd layer being an ink absorptivity layer.

Claim 4] The ink-jet record sheet according to claim 3 characterized by an ink absorptivity layer having a porous structure.

Claim 5] An ink-jet record sheet given in any 1 term of the claims 1-4 characterized by containing the same organic macromolecule as what the 1st layer contains an organic macromolecule and the 2nd layer contains in the 1st layer.

Claim 6] An ink-jet record sheet given in any 1 term of the claims 1-5 characterized by the 1st layer containing polyvinyl alcohol.

Claim 7] An ink-jet record sheet given in any 1 term of the claims 1-6 to which coating mass of the 1st layer is characterized by being 0.03 g/m<sup>2</sup> - 0.4 g/m<sup>2</sup>.

Claim 8] An ink-jet record sheet given in any 1 term of the claims 1-6 to which the 2nd layer thickness is characterized by 0.5-micrometer or more being 50 micrometers or less.

Claim 9] An ink-jet record sheet given in any 1 term of the claims 1-6 to which the 1st layer thickness is characterized by 0.03-micrometer or more being 0.4 micrometers or less.

Claim 10] An ink-jet record sheet given in any 1 term of the claims 1-6 to which the 2nd layer thickness is characterized by being 10 or more times of the 1st layer thickness of the above.

Claim 11] The manufacture method of the ink-jet record sheet characterized by preparing the 2nd layer with Young's modulus higher than the 1st layer on the 1st layer prepared on the base material.

Claim 12] The manufacture method of the ink-jet record sheet according to claim 11 characterized by being formed when the 2nd layer applies ink absorptivity layer application liquid and dries this.

Claim 13] The manufacture method of the ink-jet record sheet according to claim 11 or 12 characterized by preparing the 1st layer on a base material before the 2nd layer is formed.

Claim 14] The manufacture method of an ink-jet record sheet given in any 1 term of the claims 11-13 characterized by the 1st layer being an under-coating layer.

Claim 15] The manufacture method of the ink-jet record sheet according to claim 11 characterized by being manufactured by carrying out the simultaneous multistory application of the 2nd layer with the 1st layer.

Claim 16] The manufacture method of the ink-jet record sheet according to claim 15 characterized by carrying out a simultaneous multistory application using a curtain coating machine.

Claim 17] The manufacture method of the ink-jet record sheet according to claim 15 characterized by carrying out a simultaneous multistory application using a slide coating machine.

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Translation done.]

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 \*\*\*\* shows the word which can not be translated.  
 In the drawings, any words are not translated.

## DETAILED DESCRIPTION

## Detailed Description of the Invention]

0001]

The technical field to which invention belongs] this invention relates to the ink-jet record sheet which had few cracks, and was excellent in paint film intensity, and was excellent in gloss in more detail about an ink-jet record sheet.

0002]

Description of the Prior Art] An ink-jet recording method has little noise, high-speed record is possible, and even a possible hatchet, various printers, the plotter of multiple-color-izing, etc. are various, and it is used.

0003] An ink-jet record sheet has the common structure which painted the ink absorptivity layer on base materials, such as paper of fine quality, various kinds of papers, such as coat paper, or a synthetic paper, cloth, and plastic film, through the under-coating layer.

0004] Since an ink absorptivity layer satisfies the fixing nature of ink at the same time it gathers voidage and raises ink absorptivity, what the thing containing the solid-state particle is a subject, mixed these solid-state particle with the high molecular compound as a binder, and was distributed is common as an ink absorptivity layer. In order to raise the adhesive property of the above-mentioned base material and an ink absorptivity layer in order to apply this uniformly and, an under-coating layer can be painted on a base material, and an ink absorptivity layer can be applied on this.

0005] It is the purpose which improves an adhesive property and is uniformly applied as these under-coating layers, and the under-coating layer which consists of water-soluble polymer conventionally has been used. Since many water-soluble polymer is too used as a binder of an ink absorptivity layer, although this is because this and compatibility are good, it has many things which use gelatin as an under-coating layer also in these. However, the shrinkage force at the time of the paint film dryness generated in the interface of an under-coating layer and an ink absorptivity layer could not fully be eased, but the paint film (ink absorptivity layer) exfoliated from the base material, and the thing using conventional gelatin as an under-coating layer had the fault that a crack arose.

0006]

Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is obtaining the glossy good ink-jet record sheet which generating of a minute crack was reduced at the time of dryness, and was excellent in paint film intensity.

0007]

Means for Solving the Problem] The purpose of this invention is attained by the following meanses.

0008] 1. Ink-jet record sheet which has the 2nd layer prepared so that the 1st layer and this which were prepared on base material might be touched, and is characterized by Young's modulus of the 1st layer being lower than Young's modulus of the 2nd layer.

0009] 2. Ink-jet record sheet given in the above 1 characterized by the 1st layer being under-coating layer.

0010] 3. The above 1 characterized by the 2nd layer being ink absorptivity layer, or ink-jet record sheet given in 2.

0011] 4. Ink-jet record sheet given in the above 3 characterized by ink absorptivity layer having opening structure.

0012] 5. Ink-jet record sheet given in any 1 term of the above 1-4 characterized by containing the same organic macromolecule as what the 1st layer contains organic macromolecule and the 2nd layer contains in the 1st layer.

0013] 6. Ink-jet record sheet given in any 1 term of the above 1-5 characterized by the 1st layer containing polyvinyl alcohol.

0014] 7. Ink-jet record sheet given in any 1 term of the above 1-6 with which coating mass of the 1st layer



characterized by being 0.03 g/m<sup>2</sup>-0.4g/m<sup>2</sup>.

015] 8. Ink-jet record sheet given in any 1 term of the above 1-6 with which the 2nd layer thickness is characterized by 0.5-micrometer or more being 50 micrometers or less.

016] 9. Ink-jet record sheet given in any 1 term of the above 1-6 with which the 1st layer thickness is characterized by 0.03-micrometer or more being 0.4 micrometers or less.

017] 10. An ink-jet record sheet given in any 1 term of the above 1-6 with which the 2nd layer thickness is characterized by being 10 or more times of the 1st layer thickness of the above.

018] 11. The manufacture method of the ink-jet record sheet characterized by preparing the 2nd layer with Young's modulus higher than the 1st layer on the 1st layer prepared on the base material.

019] 12. The manufacture method of an ink-jet record sheet given in the above 11 characterized by being dried when the 2nd layer applies ink absorptivity layer application liquid and dries this.

020] 13. The above 11 characterized by preparing the 1st layer on a base material before the 2nd layer is dried, or the manufacture method of an ink-jet record sheet given in 12.

021] 14. The manufacture method of an ink-jet record sheet given in any 1 term of the above 11-13 characterized by the 1st layer being an under-coating layer.

022] 15. The manufacture method of an ink-jet record sheet given in the above 11 characterized by being manufactured by carrying out the simultaneous multistory application of the 2nd layer with the 1st layer.

023] 16. The manufacture method of an ink-jet record sheet given in the above 15 characterized by carrying out a simultaneous multistory application using a curtain coating machine.

024] 17. The manufacture method of an ink-jet record sheet given in the above 15 characterized by carrying out a simultaneous multistory application using a slide coating machine.

025] Hereafter, this invention is explained in detail. As a result of this invention persons' repeating examination wholeheartedly in view of the above-mentioned situation, it came to make this invention. That is, as a reason which produces a minute crack at the time of these dryness, it is for stress to occur in the interface of an ink absorptivity layer and an under-coating layer at the time of dryness, and found out that a crack decreased greatly by easing this. According to this invention, for the stress relaxation at the time of dryness of the above-mentioned under-coating layer and an ink absorptivity layer, it is effective to use an under-coating layer with more low Young's modulus, and setting up so that the Young's modulus of an under-coating layer may become small compared with the Young's modulus of an ink absorptivity layer brings about an effect. It follows, for example, replaces with a gelatin under-coating layer, and there is an effect with big using the low polyvinyl alcohol of Young's modulus etc. more.

026] Separately, the Young's modulus of each layer applies each application liquid to the front face of the board of polypropylene, after dryness, it removes a film, produces a film with a thickness of 200 micrometers, and measures Young's modulus at a room temperature (25 degrees C, 60%RH).

027] The range of 50-100kg /of Young's modulus of an ink absorptivity layer is [ mm ]<sup>2</sup>, and it is [ the Young's modulus of an under-coating layer ] desirable to set 20-100kg /as the range of 2 mm smaller than this.

028] Thereby, a crack is decreased and the ink-jet record sheet excellent in glossiness with strong paint film intensity is obtained.

029] What is necessary is to choose a well-known material, respectively and just to combine it so that the relation to such a relation of Young's modulus may become in order to make Young's modulus of an under-coating layer lower than the Young's modulus of an ink absorptivity layer. Moreover, you may prepare application liquid by putting the matter for adjusting Young's modulus into the application liquid of each layer. Thus, although you may put into an ink absorptivity layer and you may put into an under-coating layer when putting in the matter for adjusting Young's modulus, putting into an under-coating layer is desirable so that the ink absorptivity of an ink absorptivity layer may not be reduced if possible.

030] Moreover, if the amount of coating of the under-coating layer by these polyvinyl alcohol etc. has the desirable range of 0.03 g/m<sup>2</sup> - 0.4 g/m<sup>2</sup> with the mass at the time of dryness and there are few amounts of these coating, stress relaxation will not fully be made, but surface gloss will be lost if many [ conversely / so ]. Moreover, an under-coating layer has 0.03 micrometers - desirable 0.4 micrometers by the same reason.

031] The thing of the polymerization degree 100-5000 of the 70 - 100% of the degrees of saponification which is preferably used for this invention and by which polyvinyl alcohol is obtained from polyvinyl acetate is used. The degree of saponification is desirable and polymerization degree is 1000 or more things 85% or more. As these polyvinyl alcohol, a commercial thing can come to hand more easily than for example, Kuraray Co., Ltd., a Japanese synthetic chemistry, etc. Denaturation polyvinyl alcohol, such as anion

naturation polyvinyl alcohol which has the polyvinyl alcohol which carried out cation denaturation of the carboxyl denaturation polyvinyl alcohol, the end alkyl polyvinyl alcohol, the silanol denaturation polyvinyl alcohol, and the end other than the general polyvinyl alcohol which understands polyvinyl acetate an added part and is obtained, and an anion denaturation machine, is also contained in the polyvinyl alcohol described by this invention. Especially, silanol denaturation polyvinyl alcohol is desirable.

[032] Although the ink absorptivity layer of the structure where ink absorption is made by having opening structure in \*\*\*\* and ink being held mainly in the opening also in the swollen type ink absorptivity layer which a binder mainly swells an ink absorptivity layer and absorbs ink is sufficient, as for an ink absorptivity layer, it is desirable to have opening structure. Although a crack tends to be made by having opening structure, a crack can be remarkably reduced by applying this invention. Desirable voidage is 40 - 80%, and especially desirable. [ 50 - 70% of ] Voidage is obtained by the following formulas here.

[033]

voidage = void-volume/(paint film thickness x unit area)

void volume (cc/m<sup>2</sup>) can be measured by the method of mercury penetration based on J.TAPPI paper pulp test-method No.48-85. Expressing application thickness per cm, a unit area is 21m.

[034] There are few worries about the crack of the ink absorbing layer which sufficient ink rate of absorption will be obtained if voidage is 40% or more, and will be easy to generate at the time of manufacture in damp environment and storage etc. especially if it is 80% or less.

[035] Although the solid-state particle is included in order for an ink absorptivity layer to gather voidage, to raise ink absorptivity and to satisfy the fixing nature of ink simultaneously again, as a solid-state particle used for these ink absorptivity layer, silicate, such as a calcium carbonate, a calcium sulfate, a magnesium hydroxide, a basic magnesium carbonate, an alumina, an aluminum hydroxide, a synthetic silica, and a calcium silicate, an aluminum hydroxide, a barium sulfate, titanium oxide, a zinc carbonate, a zinc oxide, oxidized silicon, a zeolite, RITOBON, etc. are mentioned, for example.

[036] As a water-soluble organic high molecular compound for distributing these solid-states particle and repairing an ink absorptivity layer For example, gelatin, a polyvinyl pyrrolidone, sodium polyacrylate, polyvinyl alcohol and its denaturation object, starch, and its denaturation object, An oxidized starch, therification starch, vinyl acetate, a carboxymethyl cellulose, Cellulosics, such as a hydroxyethyl cellulose, casein, soybean protein, Silyl denaturation polyvinyl alcohol etc.; A maleic-anhydride resin, a styrene-butadiene copolymer, conjugated-diene system copolymer latexes [ , such as a methyl methacrylate-butadiene copolymer, ]; — acrylic polymer latexes [ , such as a polymer of an acrylic ester and a methacrylic ester, or a copolymer, ]; — vinyl system polymer latexes [ , such as an ethylene-vinyl acetate copolymer, ]; — for the functional-group denaturation polymer latex by functional-group content monomers, such as a carboxyl group of these various polymers; water-soluble organic macromolecules (water-soluble polymer), such as heat-curing synthetic-resin systems, such as melamine resin and a urea-resin, etc. are mentioned, and mixed use is also possible at two or more sorts.

[037] The solid-state particle used for an ink absorptivity layer could be compounded under existence of a water-soluble organic high molecular compound which was indicated, others, for example, JP,9-164761,A. above ]

[038] In this case, especially as an inorganic substance which can be used as a raw material for composition of the aforementioned solid-state particle, although not limited, it is desirable to use metal alkoxides, such as a salt of silicon, such as an ulmin acid alkali-metal salt like an aluminum sulfate, an aluminium nitrate, an aluminum chloride and an aluminum salt like the prototype, a sodium aluminate, or a potash salt or solution of the both water-soluble aluminium compound, and silicate of soda, or aluminum isopropoxide, and a tetrapod ethoxy silane, etc.

[039] A solid-state particle has [ particle size ] desirable 0.003-2 micrometers, 0.005-0.5 micrometers is more desirable, 0.05-0.5 micrometers is still more desirable, and 0.05-0.2 micrometers is still more desirable.

[040] The mean particle diameter of a non-subtlety particle observes the cross section and front face of the particle itself or an opening layer with an electron microscope, and is called for as the arithmetic average value (number average) in quest of the particle size of 100 arbitrary particles. The particle size of each [ here ] is expressed with the diameter when assuming a circle equal to the projected area.

[041] As for a solid-state particle, what has pore from the relation between the rate of absorption of ink or absorption capacity is desirable, and average pore size has [ 40-200A ] desirable still more desirable 20-400A.

[042] 0.5 - 5.0 ml/g of pore volume is desirable, and its 1.0 - 2.5 ml/g is still more desirable.

043] Moreover, about the configuration of pore, the gourd type with a small tortuosity factor in which it is form, the straight-line-like thing is better for, and the shape of an ink bottle with a narrow entrance and middle are narrow, the form which has wound are not desirable from viewpoint of the rate of sorption of ink.

044] Although ink absorptivity layer thickness is strictly determined by the kind of the ink used or its vent, the amount of ink, etc., its thickness of 5-50 micrometers is desirable. Moreover, when there are two or more ink absorptivity layers, it is desirable that those sum totals are 5-50 micrometers. Since there is possibility that absorptivity may become high too much, even coloring matter may carry out absorption support, and the concentration of an image may fall in absorptivity's running short and an image's bleeding, not fulfilling the aforementioned range, and exceeding the aforementioned range conversely, neither is desirable.

045] Since it becomes impossible for this solid-state particle to fully appear highly minute quality of image when there are not much too many binders, naturally the operating rate of a solid-state particle and a binder is not desirable. for this reason, the amount of the binder used – the total amount of this solid-state particle receiving – a 0 - 50 mass % grade – further – it is appropriate to do 5-20 mass % adoption of

046] In this invention, a dispersant [ of the solid-state particle of this invention ], thickener, fluid improvement agent, defoaming-agent, foam-suppressor, release agent; foaming agent; penetrating agent, coloring color, color-pigment, fluorescent brightener, ultraviolet ray absorbent, antioxidant, antiseptics, \*\* storcycle agent, deck-watertight-luminaire-ized agent, humid paper reinforcing agent, and dryness paper reinforcing agent etc. can also be suitably blended as an additive of others which can be added in an ink absorptivity layer.

047] In the ink-jet record sheet of this invention, an ink absorptivity layer does not necessarily need to consist of a monostromatic, this may be constituted from two or more layers, and the Young's modulus of a coat under-coating layer and the touching layer should just fill the relation of this invention at least among the under-coating layer and an ink absorptivity layer in this case. the ink absorptivity layer (layer prepared in the 1st layer) of plurality [ one / most desirable ] – the Young's modulus of an under-coating layer (the 1st layer) is a low case from which Young's modulus

048] As a base material used in this invention, paper or a thermoplastics film, a synthetic paper, synthetic-resin lamination paper like the paper base material which laminated both sides with polyethylene, and the sheet-like matter like the nonwoven fabric which made wood fiber and the synthetic fiber the subject are mentioned. In the case of paper, it may not contain [ independent or combined use use of sizing compounds, such as additive-free / of an inner \*\* sizing compound / addition or additive-free /, a neutralize agent, a polymer sizing compound, and an acid sizing compound, content of a loading material, or ], and the existence of size press does not restrict it at all, either. Although a conventionally well-known pigment is used and an independent region can be used together as inner \*\*\*\*\* of a paper base material, and white pigments For example, a precipitated calcium carbonate, whiting, a kaolin, clay, Talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, Zinc sulfide, a zinc carbonate, a satin white, aluminum silicate, the diatom earth, A calcium silicate, a magnesium silicate, a synthetic silica, an aluminum hydroxide, A white inorganic pigment like an alumina, a lithopone, a zeolite, a magnesium carbonate, and a magnesium hydroxide, An organic pigment like a styrene system plastics pigment, an acrylic plastics pigment, polyethylene, a microcapsule, a urea-resin, and melamine resin etc. is mentioned. Furthermore, although it is desirable that a neutral-size agent and a loading material are contained, and the ratio of wood pulp/loading material is 90 - 70 mass % / ten to 30 mass %, and weighing capacity is 60 - 120 g/m<sup>2</sup> when this base material is paper, a limit is not received at all.

049] As the production method of the ink-jet record sheet of this invention After obtaining the aforementioned base material sheet, by a DIP application method, a bar coat method, the blade application method, the air knife method, the slide coater, curtain application, etc. Although these layers may be applied and produced one by one so that it may say that an under-coating layer is applied and the aforementioned ink absorptivity layer is applied on it after dryness, preferably For example, a curtain coating machine which was indicated by JP,49-24133,B and JP,6-183132,A, Moreover, it can carry out simultaneous multistory [ of an under-coating layer and the ink absorptivity layer ] by slide coating machine which was indicated by U.S. Pat. No. 2,761,419 and 2,761,791, 5,849,363, 5,843,530, and 5,736,067.

050] Although a curtain coating machine has a large gap from a lip to an application side and is a few method of applying the application defect by the aggregate or the foreign matter, it can make a free-fall curtain able to form and a simultaneous multistory application can be carried out from the synthetic layer which passed two or more fluid beds by which simultaneous multistory is carried out in this free-fall layer so

0.3g of sulfuric acids and carried out amalgam decomposition at 50 degrees C for 75 hours (it carries out applying ultrasonic distribution slightly at this time), it was made to condense until it was set to 750g, and a solid-state particle (gelatin-sol A) of yellow white was obtained. 062] The gelatin 10 mass % solution was added to the solid-state particle (gelatin silica sol A) produced by this method, the solid-content ratio of a silica/gelatin was adjusted to 5/1, and these dispersion liquid are obtained as coating liquid.

063] The dryness application was carried out so that a bar coating machine might be used and the thickness after dryness might be set to 30 micrometers on the base material which painted the aforementioned gelatin under-coating layer in the above-mentioned ink absorptivity layer coating liquid 1-3, and sample No.1-3 of Table 1 in which the ink absorptivity layer which has opening structure was prepared are produced.

064] Subsequently, both sides of the paper base material of the aforementioned 80 g/m2 It covers with polyethylene (130 micrometers in thickness). In the polyethylene layer by the side of an ink acceptance layer, a titanium dioxide The undercoating layer which is from the polyvinyl alcohol (PVA KL-117 (Kuraray Co., Ltd. make)) of 0.1 g/m2 (0.1 micrometers of thickness after dryness) on the titanium-dioxide content of the reflective base material of which 7 mass % content was done to polyethylene in the amount of coating is given. The aforementioned coating liquid 1-3 was applied on it, and the ink-jet record sheet of sample No.4-12 of Table 1 which was able to prepare the ink absorptivity layer which has opening structure as produced. It prepared so that it might become Young's modulus as added a boric acid in the under-coating layer of polyvinyl alcohol in that case and shown in Table 1.

065] Separately, the Young's modulus of each layer applied each application liquid to the front face of the board of polypropylene, after dryness, it removed the film, produced the film with a thickness of 200 micrometers, and measured Young's modulus under 25 degrees C, and 60% conditions of RH. It pulled for measurement and the testing machine (an incorporated company cage en tech, tensilon RTC-1210A) was used.

066] Moreover, the voidage of the ink absorptivity layer of the produced sample was computed from void-volume/(thickness x unit area of a paint film) by measuring a void volume (cc/m2) using method of mercury penetration based on J.TAPPI paper pulp test-method No.48-85. In here, application thickness is expressed per cm and a unit area is 2 1m.

067] About the crack of a paint film, cyano printing of this was actually carried out, the microphotography was taken by one 50 times the scale factor of this about the printing section, and viewing estimated using this photograph.

068] x in which generating of \*\*:crack generating of O:crack, as for an error criterion, generating of X:crack is not accepted to be at all is hardly accepted to be is accepted partially: The result which observed usually about the generating situation of the crack after the Young's modulus of each class and application dryness is shown in the following table 1 where cracks are occurring frequently.

069]

Table 1]

試料 No.	インク吸収性 層塗工液	下引き層	インク吸収性層 ヤング率 kg/mm <sup>2</sup>	下引き層 ヤング率 kg/mm <sup>2</sup>	ひび割れ	空隙率	微粒子/バインダー	備 考
1	1	G E L	63	140	×	63	5/1	比 較
2	2	G E L	65	140	×	65	10/1	比 較
3	3	G E L	61	140	×	59	5/1	比 較
4	1	P V A	63	70	△	63	5/1	比 較
5	2	P V A	65	70	△	65	10/1	比 較
6	3	P V A	61	70	△	59	5/1	比 較
7	1	P V A	63	55	◎	63	5/1	本発明
8	2	P V A	65	55	◎	65	10/1	本発明
9	3	P V A	61	55	◎	59	5/1	本発明
10	1	P V A	63	30	◎	63	5/1	本発明
11	2	P V A	65	30	◎	65	10/1	本発明
12	3	P V A	61	30	◎	59	5/1	本発明

0070] It ranked second example 2 and the polyvinyl alcohol under-coating layer to which the amount of coating was changed as it was indicated in Table 2 as sample No.7 of Table 1 and the same ink absorptivity layer coating liquid at the base material of an example 1 was applied. When the Young's

modulus of this polyvinyl alcohol layer measured according to the aforementioned measuring method, it was [ mm ] 2.55kg / . Moreover, 63% of Young's modulus of an ink absorptivity layer was [ mm ] 2.71] The ink absorptivity layer coating liquid 1 of an example 1 was applied on this base material, and the generating situation of a crack as well as an example 1 was too observed similarly after dryness. 72] Moreover, also with gloss, the ink-jet sheet was observed visually and two stages of what has good gloss (O), and the thing (\*\*) in which gloss is blunt and cloudiness is accepted were evaluated. 73] The above result is shown in Table 2.

74]

Table 2]

塗工量 g / m <sup>2</sup>	ひび割れ	光沢
0.01	○	○
0.03	◎	○
0.1	◎	○
0.3	◎	○
0.5	◎	△

75] The ink-jet record sheet of this invention is understood that there are few cracks and glossiness is so good as mentioned above.

76] The simultaneous multistory application of the polyvinyl alcohol layer coating liquid which added the boric acid of a minute amount and was prepared was carried out in the amount of coating same on the base material used in the example 1 in the curtain coating machine indicated by drawing 1 of JP,6-3132,A viscosity and after [ , such as surface tension etc. , ] adjusting as an example 1, respectively so that 40kg /of Young's modulus of the example 3 above-mentioned coating liquid 1 and the film after an application might be set to 2 mm, and the ink-jet record sheet was produced.

77] As a result of printing cyano ink like examples 1 and 2 to this thing and observing a crack visually about the printing section, a crack was not observed but it was a good result.

78] It is this thing although the simultaneous multistory application of the polyvinyl alcohol layer coating liquid which added the boric acid of a minute amount and was prepared was carried out in the too same amount of coating as an example 1 on the base material used in the example 1 in the slide coating machine indicated by U.S. Pat. No. 5,849,363 after [ , such as surface tension etc. , ] adjusting, viscosity and, respectively so that 40kg /of Young's modulus of the example 4 above-mentioned coating liquid 1 and the film after an application might be set to 2 mm, and the ink-jet record sheet was produced As a result of printing cyano ink like examples 1 and 2 and observing a crack visually, a crack was not observed but the good result was shown.

79] The polyvinyl alcohol under-coating layer same on the same base material as sample No.10 of example 5 example 1 was prepared, and further, on it, the dryness thickness of each ink absorptivity layer carried out the simultaneous multistory application of the application liquid of each class using the slide applicator so that it might be set to layer [ 3rd ] layer [ 2nd ] 8 micrometers of the 1st layer of each lower shell and 17 micrometers, and 8 micrometers. In addition, prescription of class application liquid is shown below.

80] After "manufacture of titanium oxide dispersion liquid -1" mean particle diameter added in 90l. of solution which contains 10g for 150g, polyvinyl alcohol (Kuraray Co., Ltd. make-VA235) 500g, and the defoaming agent SN381 made from SANNOBUKO, Inc. and distributed 20kg of titanium oxide which is about 0.25 micrometers, and the sodium tripolyphosphate of pH=7.5 with the high-pressure homogenizer (the Sanwa Industries make), 100l. was made to the whole quantity and uniform titanium oxide dispersion liquid -1 were obtained.

81] After carrying out suction distribution at a room temperature into the 620l. pure water to which the mean particle diameter of "manufacture of silica dispersion liquid -1" primary particle adjusted to pH=2.5 aqueous-phase method silica (Japanese Aerosil Industries make : A300) 125kg which is about 0.007 micrometers with the nitric acid using the jet stream inductor mixer TDS by Mitamura \*\*\*\* Industries, 694l. was made to the whole quantity with pure water.

82] It added stirring 69.4l. of silica dispersion liquid -1, and subsequently, 7.0l. of solution containing 30g of boric acids and 230g of boraxes was added in 18l. (pH=2.3) of solution which contains 1.63kg, ethanol 2.2l., and n-propanol 1.5l. for "manufacture of silica dispersion liquid -2" cation polymer P-1, and the 1g of the aforementioned defoaming agents SN381 was added in it.

83] The high-pressure homogenizer by Sanwa Industries distributed this mixed liquor, 97l. was made to